

# TITANIUM DIOXIDE PIGMENT COMPOSITION

## Cross Reference To Related Application

This application is based on and claims priority from United States  
5 Provisional Patent Application Serial No. 60/240,190, filed October 11, 2000.

## Background

### 1. Field of the Invention

This invention relates to the field of  $\text{TiO}_2$  pigment compositions. More  
10 particularly, this invention pertains to pigment compositions composed of  $\text{TiO}_2$  and barium  
sulfate in amounts which provide enhanced opacity and brightness to substrates containing  
the compositions.

### 2. Background of the Invention

15  $\text{TiO}_2$  is a white pigment which has a high index of refraction and excellent  
light diffusing properties. It is used as a pigment for various substrates, such as, plastics,  
paper and coating compositions, including paints. See, for example, U.S. Patent 6,267,812,  
the contents of which are incorporated herein by reference.

20  $\text{TiO}_2$  is generally found in two different crystalline forms referred to as  
anatase and rutile. Both forms may be used as an opacifying agent for a variety of  
substrates. The  $\text{TiO}_2$  may be mixed with water to form a slurry which can be incorporated  
into or onto the substrate by mixing with the particular material making up the substrate or  
coating onto the surface of the substrate. Alternatively, for use in non-aqueous systems,

such as a plastic or polymeric substrate, the  $\text{TiO}_2$  may be added directly to the substrate in a suitable form as is well known in the art.

However,  $\text{TiO}_2$  presents a number of problems with respect to its use.

5 Specifically, it is relatively expensive and exhibits a propensity to undergo autoflocculation; namely, it agglomerates both in the dry state as well as when slurried in water which makes it difficult to maximize its opacifying capacity (See U.S. Patent No. 5,705,033.)

10 In order to ameliorate such problems,  $\text{TiO}_2$  has been mixed with other pigment materials, e.g., cationic polymers, saccharides, siloxanes, kaolin; clays, and the like. However, the addition of such materials deteriorates the capability of the  $\text{TiO}_2$  with respect to its opacification properties and generally have only partially alleviated the agglomeration problem.

15 Barium sulfate is a white water insoluble compound which has also been used in pigment compositions, or x-ray contrast agents. It may be obtained in a natural state as well as synthetically as a material known as blanc fixe. However, it does not exhibit significant opacification properties but does provide "brightness" to compositions to which it is added.

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For purposes of this application, the terms "opacity" or "opacifier" relate to the ability or property of being or rendering a substrate impervious to light rays so that it not transparent. Thus, with respect to  $\text{TiO}_2$  having opacifier or opacification properties, it is meant that when applied onto or incorporated into a substrate, it increases blockage of light  
25 rays.

As used herein, the term "brightness" or "brightening" refers to the ability of a material to reflect light thereby increasing its intensity. Thus, generally, it is perceived as light which is reflected from a surface.

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#### Summary of the Invention

I have discovered that the above disadvantages of  $\text{TiO}_2$  compositions can be decreased by the use of a pre-prepared composition composed of titanium dioxide and barium sulfate wherein the amount of barium sulfate is sufficient to prevent the agglomeration of the  $\text{TiO}_2$ . Moreover, I have discovered that the addition of this anti-  
10 agglomeration effective amount of barium sulfate does not detract from the opacification properties of the  $\text{TiO}_2$  and in addition, assists in providing brightness characteristics to the overall pigment composition.

Either rutile or anatase  $\text{TiO}_2$  may be used in the inventive composition. The  
15 barium sulfate may be in the form of naturally obtained barium sulfate, i.e., natural barytes, or synthetic barium sulfate, namely, blanc fixe.

The inventive composition may be provided either as a dry mixture or in the form of a slurry which may then be diluted or used as is for the particular substrate to be  
20 opacified.

#### Detail Description of the Invention

The pigment composition of the present invention contains titanium dioxide and barium sulfate wherein the amount of barium sulfate is sufficient and effective to

reduce the agglomeration of the titanium dioxide when the composition is formed into an aqueous slurry.

As used herein, the "total solids content" means the weight of all components in the absence of water. This is sometimes referred to as the dry weight of the composition. Generally, the pigment composition of the present invention as a slurry has a total solids content or dry weight in the range from about 65.0 to 80.0, and preferably is from about 70.0 to 73.0 percent by weight based on the total weight of the slurry composition.

Particularly, I have found that the effective amount of barium sulfate may be added to the composition in accordance with the invention amounts from about 5.0 up to about 35.0 percent by weight based on the weight of the total solids of the composition and the amount of  $\text{TiO}_2$  may be in the range from about 95.0 to 65.0 percent by weight based on the weight of the total solids of the composition. Thus, even at levels of about 5.0 percent by weight, an economic advantage can be realized by virtue of the decreased amount of  $\text{TiO}_2$  in the composition. At barium sulfate levels above about 35.0 percent by weight, the opacifying capacity of the  $\text{TiO}_2$  in the composition begins to decrease. However, the effects on the opacifying properties of the  $\text{TiO}_2$  may also be dependent on the particular substrate so that, in certain substrates and/or end uses, the opacifying capability of the  $\text{TiO}_2$  may be satisfactory even at barium sulfate levels above 35.0 percent by weight.

Preferably, the amount of barium sulfate is in the range from about 30.0 to 24.0 percent by weight and the  $\text{TiO}_2$  is in the range from about 70.0 to 76.0 percent by weight based on the total weight of the solid content of the composition.

The composition may further contain conventional additives of the type which are well known in the art. Typically, these may constitute materials which are

defoamers, dispersants, biocides, pH adjustment agents and a combination of these ingredients. One skilled in this art is well aware of all of the various types of additives which may be utilized and usually, the nature and type of additive used depends on the specific end use of the pigment composition and the particular substrate in which it will be used.

Preferably, an additive is used in an amount from about 0.5 to 3 percent by weight, based on the weight of the total solids of the composition.

Typical additives which may be utilized in the inventive composition include materials, such as, dimethyl polysiloxane, octamethylcyclotetrasiloxane, anionic polyacrylate, polyglycolethers, fumed silica ethers, petroleum hydrocarbons, acrylic polymers, triethanolamine, bicyclic oxazolidines, 1,2-benzisothiazolin-3-on, sodium hydroxide as well as combinations of these ingredients.

A particularly preferred composition for use in opacification of paper products is composed of from about 74.5 to 75.5 percent by weight of titanium dioxide and from about 24.5 to 25 percent by weight blanc fixe, the weights being based on the total solids weight of the composition. In this particularly preferred embodiment, the composition is in the form of an aqueous slurry having a total solids content in the range from about 71.0 to 72.9 percent by weight based on the total weight of the slurry composition.

The inventive composition preferably, in aqueous slurry form, has a pH of from about 7.0 to 10.0, a maximum 325 sieve residue of fifty parts per million, and a

Brookfield viscosity of about 200 to 800 as measured with a #4 spindle at 100 rpm at ambient temperature.

The inventive composition may be mixed in a dry state and sold as a powder  
5 for subsequent slurring or slurried in water and sold in this form. Typical uses for the  
inventive composition are in the manufacture of a variety of substrates in order to increase  
their opacity and brightness. As used herein the word "substrates" refers to those materials  
which generally require some level of opacification for their ultimate end use. These  
substrates may be in a variety of forms such as films, sheets, shaped elements, e.g., shaped  
10 components for use in machinery, household goods, toys, automobiles, aircraft, and the like.  
The substrates generally may be composed of papers, plastics as well as a variety of  
coatings in which pigments are generally used, for example, paints, inks and stains.

The inventive composition is particularly suitable for use in the paper  
15 industry wherein it is mixed with the pulp at some point during the conventional paper  
making process. In addition, the inventive composition may also be coated onto paper at an  
appropriate point in the paper making process. In the same manner, it may be used as a  
coating for the other aforementioned substrates in order to create an opacifying layer  
thereon. One skilled in this art fully understands how to use such a pigment composition in  
20 connection with the particular product with which that person is dealing. No special  
techniques are required for use of the inventive pigment composition and conventional  
procedures may be utilized in all respects.

The inventive composition exhibits a unique effect of dispersing the titanium  
25 dioxide particles and maintaining their separation as a result of the spacing provided by the

barium sulfate when the composition is formed into an aqueous slurry. This makes the composition particularly suitable for use in paper coatings and wet end paper applications.

The inventive composition provides a number of additional advantages in particular in manufacture of paper as follows:

1. It provides increased retention of the inventive composition by the substrate.

2. The invention allows for the use of higher amounts of increased solids in a slurry which lowers the transportation cost.

3. The viscosity of the inventive slurry is improved to facilitate handling both in tank truck or rail car loading and unloading using pumping systems.

4. The inventive composition allows paper producers to use a choice of fillers for the paper beyond the normal array of clay materials in the conventional "acid" process.

5. The inventive composition has a reduced abrasiveness as compared to a 100 percent titanium dioxide composition. This reduces the overall wear in the paper making equipment and a reduction in the abrasiveness of the furnish. Blanc fixe has a hardness rating of 3.0 (moh's) hardness whereas titanium dioxide has a moh's hardness of 5.5 to 7.0. The inventive composition provides increased gloss, i.e., shine, in paper coating or allows increased productivity in the speed of calendaring of the paper while maintaining the same gloss as would have been obtained for the use of a coating which did not contain the inventive composition.

6. Higher relative bulk density is obtained with the present invention which further results in increased paper weight and strength.

The properties of the composition referred to herein above were determined as follows:

Determination of total solids of inventive slurry

5 About 3g of slurry weighed to the nearest mg were placed in a tared crucible and then dried in a microwave oven at full power for two minutes to remove water. The crucible was then subjected to calcination temperatures to carbonize organics in the composition. The crucible was then cooled and reweighed. The percent of solids was calculated as the dried weight of the crucible contents divided by the wet weight and  
10 multiplied by 100.

Viscosity determination of the inventive composition

A Brookfield viscometer model RV with a #4 spindle was used. A standard one quart retainer sample jar was filled to the top with a sample of the slurry. The sample  
15 was then allowed to rest for one hour at ambient temperature. Thereafter, the spindle was inserted until the level of the slurry was at the emersion groove of the spindle shaft. Viscosity measurement was conducted using a standard procedure with a Brookfield viscometer at both 50 and 100rpm.

20 pH Determination of TiO<sub>2</sub> Slurry

A pH meter was utilized capable of measuring the pH to 0.1 units or better was used. The pH meter was checked with buffered reference solutions having a pH of 7 and a pH of 10 and calibration was carried out if necessary. The electrodes were then introduced into the slurry and the slurry was gently agitated to ensure a thorough wetting  
25 and the pH was read to the nearest 0.1.



### Determination of 325 Mesh Residue of the Inventive Slurry

Approximately 200g of the slurry was weighed into a tared 250ml beaker weighed to the nearest 0.1g. The slurry was poured through a 325 mesh sieve using gentle tapping under a stream of water. Any slurry remaining in the beaker was washed out with water onto the screen and then the material under the screen was washed under running water until the sieve ran clear.

The residue on the screen was further washed and transferred to a tared aluminum foil weighing dish using a stream of isopropyl alcohol. The excess isopropyl alcohol was blotted from the dish using a paper towel without disturbing the residue. The contents of the dish were then subjected to drying in a convection oven at 105°C for about 30 minutes to remove the water therefrom. The dish was removed from the oven, cooled and weighed. If any question existed that the sample had not fully dried, it would be reheated, cooled and reweighed to make sure that no further weight loss occurred. The results were then determined by dividing the weight of the residue by the weight of the initial slurry and multiplying by  $1 \times 10^6$  providing results in parts per million. The amount of residue on the 325 mesh must be less than 50 ppm.